



D E C L A R A T I O N

I, Mitsuaki MURAKAMI, a national of Japan, c/o Sumitomo Chemical Intellectual Property Service, Limited, 5-33, Kitahama 4-chome, Chuo-ku, Osaka-shi, Osaka 541-8550, Japan, declare that to the best of my knowledge and belief the attached is a full, true and faithful translation into English made by me of the certified copy of Japanese Patent Application No. 2000-243302 attached thereto.

Signed this 21st day of January, 2004

Mitsuaki Murakami

Mitsuaki MURAKAMI



(54) [Title of the Invention] Phosphor-film structure, Paste for Forming This Phosphor Film, and Plasma-Display Panel Using This Phosphor Film

5 (57) [Abstract]

[Problem to Be Solved] Brightness of a phosphor film is improved by increasing the number of phosphor particles, which emit light inside a phosphor film, without increasing the number of producing processes. In addition, producing  
10 cost is reduced by decreasing the amount of expensive phosphor particles to be used.

[Means for Solving the Problem] A phosphor film 16 includes a number of phosphor particles 16a and voids 16b formed within these phosphor particles 16a. The above voids 16b occupy  
15 40-80% in the phosphor film 16 where it is defined as 100% that this phosphor particles 16a completely occupy the phosphor film 16 without any voids.

[Claims]

[Claim 1] A phosphor-film structure comprising a phosphor film (16), which includes a number of phosphor particles (16a) and voids (16b) formed within these phosphor particles (16a),  
5 wherein said voids (16b) occupy 40-80% in said phosphor film (16) where it is defined as 100% that said phosphor particles (16a) completely occupy said phosphor film (16a) without any voids.

[Claim 2] A phosphor-film structure comprising a phosphor  
10 film (36), which includes a number of phosphor particles (36a) and a number of ultraviolet-ray-transmittable particles (36b) positioned within these phosphor particles (36a), wherein voids (36c) formed within said respective particles (36a, 36b), and said ultraviolet-ray-transmittable  
15 particles (36b) occupy 40-80% in said phosphor film (36) where it is defined as 100% that said phosphor particles (36a) completely occupy said phosphor film (36) without any voids.

[Claim 3] The phosphor-film structure according to claim 2, wherein the ultraviolet-ray-transmittable particles are  
20 fluoride particles or SiO<sub>2</sub> particles.

[Claim 4] The phosphor-film structure according to claim 2, wherein the ultraviolet-ray-transmittable particles are fluoride particles coated with SiO<sub>2</sub> film.

[Claim 5] The phosphor-film structure according to claim 3  
25 or claim 4, wherein the fluoride particles are any of CaF<sub>2</sub>,

MgF<sub>2</sub>, and LiF.

[Claim 6] A paste for forming the phosphor film according to claim 1 comprising: 0.1-16% by weight of thermal-expansible microcapsules; 15-80% by weight of phosphor particles; and  
5 80-20% by weight of a mixture of resin and solvent.

[Claim 7] A paste for forming the phosphor film according to claim 1 comprising: 0.2-17% by weight of solvent-insoluble or solvent-slightly-soluble resin fine particles, which is burned out in 200-500°C and have a mean particle diameter of  
10 0.1-20 μm; 10-80% by weight of phosphor particles; and 80-20% by weight of a mixture of solvent and resin soluble therein.

[Claim 8] A paste for forming the phosphor film according to any of claims 2-5 comprising: 0.1-50% by weight of ultraviolet-ray-transmittable particles; 10-80% by weight  
15 of phosphor particles; and 80-20% by weight of a mixture of resin and solvent.

[Claim 9] A plasma-display panel comprising a phosphor film (16, 36) according to any of claims 1-5, which is formed on inner surfaces of a cell (15) surrounded by ribs (14) on or  
20 above a substrate (11).

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains] The present  
25 invention relates to a phosphor-film structure, a paste for

forming this phosphor film, and a plasma-display panel (hereinafter referred to as a PDP) using this phosphor film suitable for a phosphor-display apparatus such as a PDP.  
[0002]

5 [Related Art] A conventional phosphor-film (hereinafter also referred to as a phosphor layer) structure shown in Fig. 3 is known. The conventional phosphor-film structure is composed of a plurality of address electrodes 2 formed on a glass substrate 1 of a PDP at a predetermined interval, an  
10 insulating layer 3 formed on the glass substrate 1 so as to cover these address electrodes 2, a plurality of ceramic ribs 4 arranged on the upper surface of the insulating layer 3 at a predetermined interval, and a phosphor film 6 formed on inner surfaces of a cell 5 surrounded by these ribs 4. In order  
15 to form this phosphor film, first, phosphor particles and a vehicle (an organic binder and a solvent) are mixed at a predetermined ratio, and a phosphor paste is prepared. Next, the phosphor paste is printed on the inner surfaces of the cell, which is divided by the plurality of ceramic ribs, by  
20 a screen printing method or the like, and stands in the air at a predetermined temperature to dry. Further, the phosphor past stands in the air at a predetermined temperature so that the vehicle is burned out. Consequently, a phosphor film is obtained.

25 [0003] However, in the above conventional phosphor-film

structure, ultraviolet rays 8 generated by a plasma discharge  
7 meet only phosphor particles 6a in the surface of the  
phosphor film 6. Accordingly, phosphor particles 6a inside  
the phosphor film 6 cannot emit light (phosphor particles 6a  
5 filled in with black in Fig. 3 emit light). Therefore, there  
is a problem that its brightness is low. On the other hand,  
in order to solve the problem, in a technology related to the  
present invention, Japanese Laid-Open Publication Kokai No.  
HEI 1-274354 discloses an ultraviolet-ray excitation arc tube  
10 (hereinafter referred to as a fluorescence lamp) using a  
luminescence composition containing phosphor particles and  
fluoride of alkaline-earth metal, which are mixed or fused,  
as phosphor film. It can remarkably reduce cost of a  
luminescence composition, almost without reducing its  
15 brightness.

[0004]

[Problem to Be Solved by the Invention] In the above  
conventional fluorescence lamp disclosed in Japanese  
Laid-Open Publication Kokai No. HEI 1-274354, light with  
20 wavelengths of 254 nm and 185 nm emitted by mercury is used  
as excitation light. On the other hand, in a PDP, a phosphor  
is excited by a vacuum ultraviolet ray with a wavelength of  
147 nm generated by xenon. This light is almost absorbed by  
phosphor particles, and its transmittance is also reduced by  
25 fluoride ( $\text{BaF}_2$ ,  $\text{SrF}_2$ , etc.). For this reason, the amount of

ultraviolet ray moving into the phosphor film is much reduced,  
as compared with the phosphor film in a fluorescence lamp.  
Accordingly, there is a problem that improving its brightness  
is difficult. It is an object to provide a phosphor-film  
5 structure, a paste for forming this phosphor film, and a PDP  
using this phosphor film capable of improving brightness of  
a phosphor film by increasing the number of phosphor particles,  
which emit light inside a phosphor film, without increasing  
the number of producing processes, and of reducing producing  
10 cost by decreasing the amount of expensive phosphor particles  
to be used.

[0005]

[Means for Solving Problem] As shown in Fig. 1, a  
phosphor-film structure according to claim 1 comprises a  
15 phosphor film 16, which includes a number of phosphor  
particles 16a and voids 16b formed within these phosphor  
particles 16a, wherein the voids 16b occupy 40-80% in the  
phosphor film 16 where it is defined as 100% that the phosphor  
particles 16a completely occupy the phosphor film 16 without  
20 any voids. In a phosphor-film structure according to claim  
1, ultraviolet rays 18 generated by a plasma discharge 17  
excite phosphor particles 16a, and visible light is emitted  
when these phosphor particles deexcite to a ground state. In  
this case, since the ultraviolet rays 18 meet not only  
25 phosphor particles 16a in the surface of the phosphor film

16 but also phosphor particles 16a inside the phosphor film 16, the phosphor particles 16a inside the phosphor film 16 can emit light. As a result, the number of phosphor particles, which emit light, increases. Therefore, the phosphor film 16 with high brightness can be obtained.

[0006] As shown in Fig. 2, a phosphor-film structure comprises a phosphor film 36, which includes a number of phosphor particles 36a and a number of ultraviolet-ray-transmittable particles 36b positioned within the phosphor particles 36a, wherein voids 36c formed within the respective particles 36a, 36b, and the ultraviolet-ray-transmittable particles 36b occupy 40-80% in the phosphor film 16 where it is defined as 100% that the phosphor particles 16a completely occupy the phosphor film 16a without any voids. In a phosphor-film structure according to claim 2, ultraviolet rays 18 generated by a plasma discharge 17 excite phosphor particles 36a, and the phosphor particles 36a emit light (visible light). In this case, since the ultraviolet rays 18 can pass through the ultraviolet-ray-transmittable particles and meet not only phosphor particles 36a in the surface of the phosphor film 36 but also particles 36a inside the phosphor film 36, the particles 36a inside the phosphor film 36 can emit light. As a result, the number of phosphor particles, which emit light, increases. Therefore, the phosphor film 36 with high brightness can be obtained (phosphor particles 36a filled in



with black in Fig. 2 emit light). In addition, since the amount of expensive phosphor particles to be used can be decreased, producing cost can be reduced.

[0007] It is preferable that the above  
5 ultraviolet-ray-transmittable particles are fluoride particles or SiO<sub>2</sub> particles. In addition, when the ultraviolet-ray-transmittable particles are fluoride particles coated with SiO<sub>2</sub> film, it is possible to improve durability of the fluoride particles coated with SiO<sub>2</sub> film  
10 under plasma. Additionally, it is preferable that the fluoride particles are any of CaF<sub>2</sub>, MgF<sub>2</sub>, and LiF. Moreover, it is preferable that a plasma-display panel comprises a phosphor film 16 or 36, which is formed on inner surfaces of a cell 15 surrounded by ribs 14 on or above a substrate 11  
15 as shown in Fig. 1 and Fig. 2.

[0008]

[Mode for Carrying out the Invention] The following description will describe an embodiment 1 according to the present invention with reference to the drawing. As shown in  
20 Fig. 1, a plurality of address electrodes 12 is formed on a glass substrate 11 of a PDP at a predetermined interval, and an insulating layer 13 is formed on the glass substrate 11 so as to cover these address electrodes 12. In addition, a plurality of ceramic ribs 14 is arranged on the upper surface  
25 of the insulating layer 13 at a predetermined interval, and

a phosphor film 16 is formed on inner surfaces of a cell 15 surrounded by these ribs 14. The phosphor film 16 includes a number of phosphor particles 16a and voids 16b formed within these phosphor particles 16a, wherein the voids 16b occupy 5 40-80%, preferably 50-70% in the phosphor film 16 where it is defined as 100% that the phosphor particles 16a completely occupy the phosphor film 16 without any voids. The reason for limitation of the voids 16b within the range 40-80% is as follows. When it is less than 40%, it is difficult that 10 phosphor particles 16a inside the phosphor film 16 emit light. On the other hand, when it is more than 80%, even if phosphor particles 16a inside the phosphor film 16 emit light, since the amount of phosphor particles 16a is too small, predetermined brightness cannot be obtained. In addition, the 15 phosphor film 16 may be friable and reduce its brightness with time.

[0009] A method for producing the above phosphor film is described. First, phosphor particles, thermal-expansible microcapsules, and a mixture of resin and solvent (solvent 20 + plasticizer + dispersing agent) are mixed at a predetermined ratio, and a phosphor paste is prepared. The phosphor particles are 15-80% by weight, preferably 30-60% by weight. The thermal-expansible microcapsules are 0.1-16% by weight, preferably 1-10 % by weight. In addition, a mixture of resin 25 and solvent is 80-20% by weight, preferably 65-25 % by weight.

More concretely, the resin is 25-0% by weight, preferably 10-1% by weight, and the solvent is 80-7% by weight, preferably 60-20% by weight.

[0010] The reason for limitation of the phosphor particle  
5 within the range 15-80% is as follows. When it is less than 15% by weight, since the amount of phosphor particles is too small, predetermined brightness cannot be obtained. When it is more than 80%, it is difficult that phosphor particles inside the phosphor film emit light. The effect of the present  
10 invention cannot be sufficiently obtained when it is out of the range. Additionally, the reason for limitation of the thermal-expansible microcapsules within the range 0.1-16% is as follows. When it is less than 0.1% by weight, the voids cannot be sufficiently formed in the phosphor film. When it  
15 is more than 16% by weight, the strength of the phosphor film cannot be sufficiently obtained. Moreover, the reason for limitation of the mixture of resin and solvent within the range 80-20% by weight is as follows. When it is more than 80 % by weight, the viscosity of the paste is too low. When  
20 it is less than 20% by weight, its viscosity is too high. Therefore, predetermined film thickness cannot be obtained.

[0011] The resin is a polymer, which acts as binder, and decomposes by heat, and has high viscosity when solving in solvent. Cellulose group resin (ethyl cellulose, methyl  
25 cellulose, etc.), acrylic resin (methyl methacrylate, ethyl

methacrylate, etc.), vinyl chloride resin, phenol resin, and so on can be used as the resin. A nonaqueous solvent (organic solvents, such as an alcoholic group, an ether group, an aromatic series group, and a hydrocarbon group) can be used  
5 as the solvent. Triethylene glycol, terpineol, and so on can be used as preferable alcohols, and diethyl ether and so on can be used as preferable ether. In addition, a Linn acid group and a sulfonic acid group and so on can be used as the dispersing agent. Besides, in this specification, the above  
10 mixture of resin and solvent is occasionally referred to as a vehicle.

[0012]

Further, phosphor particles with a mean particle diameter of 3-4  $\mu\text{m}$  and specific gravity of 4-5  $\text{g/cm}^3$  for red, blue, and  
15 green are used as the phosphor particles. Particles of [(Y, Gd)  $\text{BO}_3\text{:Eu}$ ], and so on can be used as the phosphor particles for red. Particles of [ $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}$ ], and so on can be used as the phosphor particles for blue. Particles of [ $\text{Zn}_2\text{SiO}_4\text{:Mn}$ ], particles of [ $\text{BaAl}_{12}\text{O}_{19}\text{:Mn}$ ], and so on can be used as the  
20 phosphor particles for green. Furthermore, microcapsules, which include a shell of acrylonitrile group polymer and enclose hydrocarbon with low boiling point therein, with a mean particle diameter of 5-8 $\mu\text{m}$  can be used as the thermal-expansible microcapsules. Moreover, a mixture of  
25  $\alpha$ -terpineol/ethyl cellulose, the ratio by weight of which is

95/5, and so on can be used as the vehicle, for example.

[0013] On the other hand, the plurality of ceramic ribs are formed at a predetermined interval above the glass substrate by a screen printing method, a sandblast method, a dry film method, or the like so that the insulating layer is interposed between them. Next, the phosphor paste is printed on the inner surfaces of the cell, which is divided by the plurality of ceramic ribs above the above glass substrate, by a screen printing method or the like, and stands in the air at 150°C for 10 minutes to dry. In addition, a phosphor film, which contains voids with the range 40-80% therein, can be obtained by baking it with holding temperature at 520°C for 30 minutes. In this case, the thermal-expansible microcapsule expands its volume about 2-3 times at a drying process with evaporation of the solvent, such as hydrocarbon with low boiling point enclosed in the microcapsule. Additionally, since resin components in the vehicle, the thermal-expansible microcapsule, and so on are burned out at a baking process, relatively large voids are formed inside the phosphor film.

[0014] Another method for producing the phosphor film is described. First, phosphor particles, resin fine particles, and a mixture of resin and solvent (solvent + plasticizer + dispersing agent) are mixed at a predetermined ratio, and a phosphor paste is prepared. The phosphor particles are 10-80% by weight, preferably 40-60% by weight. The resin fine

particles are 0.2-17% by weight, preferably 1-10 % by weight. The reason for limitation of the phosphor particle within the range 10-80% is as follows. When it is less than 10% by weight, since the amount of phosphor particles is too small, 5 predetermined brightness cannot be obtained. When it is more than 80%, it is difficult that phosphor particles inside the phosphor film emit light. The effect of the present invention cannot be sufficiently obtained when it is out of the range. The reason for limitation of the resin fine particles within 10 the range 0.2-17% is as follows. When it is less than 0.2% by weight, it is difficult to form the voids at 40% inside the phosphor film. When it is more than 17% by weight, the void are formed 80% or more inside the phosphor film. In addition, the resin is 25-0% by weight, preferably 10-1% by 15 weight. The solvent is 80-7% by weight, preferably 60-20 % by weight.

[0015] Components of the phosphor particles, and the mixture of resin and solvent similar to the above the method for producing are used. Additionally, it is preferable that the 20 resin fine particles are solvent-insoluble or solvent-slightly-soluble, and are burned out in 200-500°C, preferably 200-400°C, and have a mean particle diameter of 1-20  $\mu\text{m}$ , preferably 0.1-10  $\mu\text{m}$ . It is preferable that the resin fine particles are formed of a resin essentially consisting 25 of elements C (carbon), H (hydrogen), and O (oxygen). For

example, polyethylene, polyethylene oxide, acrylic resin, meta-acrylic resin, cellulosic resin, polystyrene, and so on can be used. The reason for limitation of the resin fine particles within the range of the burned-out temperature 200-500°C is as follows. When it is less than 200°C, the resin fine particles are burned out at the drying process. When it is more than 500°C, it is difficult that the resin fine particles are completely burned out at the baking process. The reason for limitation of the resin fine particles within the range of the mean particle diameter 0.1-20 µm is that voids larger than the conventional thickness of a phosphor film are formed, when it is more than 20 µm. In this case, the insulating layer as a primary layer appears.

[0016] On the other hand, the plurality of ceramic ribs 14 are formed at a predetermined interval above the glass substrate 11 by a screen printing method, a sandblast method, a dry film method, or the like so that the insulating layer 13 is interposed between them. Next, the phosphor paste is printed on the inner surfaces of the cell 15, which is divided by the plurality of ceramic ribs 14 above the glass substrate 11, by a screen printing method or the like, and stands in the air at 150°C for 10 minutes to dry. In addition, a phosphor film 16, which contains voids 16b with the range 40-80% therein, can be obtained by baking it with holding temperature at 520°C for 30 minutes. Since the resin fine particles within

the phosphor particle 16a are burned out at the baking process, it is possible to form the voids 16b with a predetermined ratio inside the phosphor film 16.

[0017] In the phosphor-film structure produced by the above  
5 method, when predetermined voltage is applied between display electrodes (not shown), a plasma discharge 17 is produced inside the cell 15 as shown in Fig. 1. Ultraviolet rays 18 by this plasma discharge 17 excite the phosphor particles 16a, and the phosphor particles 16a emit light (visible light).  
10 In this case, since ultraviolet rays 18 meet not only phosphor particles 16a in the surface of the phosphor film 16 but also particles 16a inside the phosphor film 16, the particles 16a inside the phosphor film 16 can emit light. As a result, the number of phosphor particles, which emit light, increases.  
15 Therefore, the phosphor film 16 with high brightness can be obtained (the phosphor particles 16a filled in with black in Fig. 1 emit light). In addition, since the amount of expensive phosphor particles to be used are decreased, producing cost can be reduced.

20 [0018] The following description will describe an embodiment 2 according to the present invention with reference to Fig. 2. In Fig. 2, components same as or similar to those of Fig. 1 are attached with the same reference letters or numerals. In this embodiment, the phosphor film 36 formed in the cell  
25 15 surrounded by a plurality of ceramic ribs 14 includes a



number of phosphor particles 36a and a number of  
ultraviolet-ray-transmittable particles 36b positioned  
within these phosphor particles 36a. In addition, voids 36c  
formed within the respective particles 36a, 36b, and the  
5 ultraviolet-ray-transmittable particles occupy 40-80%,  
preferably 50-70% in the phosphor film 36 where it is defined  
as 100% that the phosphor particles 36a completely occupy the  
phosphor film 36 without any voids. Fluoride particles,  
preferably such as  $\text{CaF}_2$ ,  $\text{MgF}_2$ , and  $\text{LiF}$ , or  $\text{SiO}_2$  particles can  
10 be used as the ultraviolet-ray-transmittable particles 36b.  
Additionally, the reason for limitation of the rate that the  
voids 36c within the respective particles 36a, 36b, and the  
ultraviolet-ray-transmittable particles 36b occupy in the  
phosphor film 36 within the range 40-80% is as follows. When  
15 it is less than 40%, it is difficult that phosphor particles  
36a inside the phosphor film 36 emit light. When it is more  
than 80%, even if the phosphor particles 36a inside the  
phosphor film 36 emit light, since the amount of phosphor  
particles 36a is too small, predetermined brightness cannot  
20 be obtained.

[0019] A method for producing the above phosphor film is  
described. Phosphor particles,  
ultraviolet-ray-transmittable particles, and a mixture of  
resin and solvent are mixed at a predetermined ratio so that  
25 the rate that the voids 36c, and the

ultraviolet-ray-transmittable particles 36b within the particles 36a occupy in the phosphor film 36 after the drying and the baking processes is within the range 40-80%, and a phosphor paste is prepared. The phosphor particles are 10-80%  
5 by weight, preferably 20-60% by weight. The ultraviolet-ray-transmittable particles are 0.1-50% by weight, preferably 1-30% by weight. In addition, the resin is 25-0% by weight, preferably 10-3% by weight. The solvent is 80-7% by weight, preferably 60-20 % by weight. The reason  
10 for limitation of the ultraviolet-ray-transmittable particle within the range 0.1-50% is as follows. When it is less than 0.1%, it is difficult that the phosphor particles inside the phosphor film emit light. When it is more than 50% by weight, the number of phosphor particles relatively  
15 decreases, therefore predetermined brightness cannot be obtained. Processes for producing the phosphor film other than that mentioned above is almost the same manner as the embodiment 1, and their descriptions are omitted for ease of explanation.

20 [0020] In the phosphor-film structure produced by the above method, when predetermined voltage is applied between display electrodes (not shown), a plasma discharge 17 is produced inside the cell 15 as shown in Fig. 2. Ultraviolet rays 18 by this plasma discharge 17 excite the phosphor particles 16a,  
25 and the phosphor particles 36a emit light (visible light).

In this case, since ultraviolet rays 18 meet not only phosphor particles 36a in the surface of the phosphor film 36 but also the particles 36a inside the phosphor film 36, the particles 36a inside the phosphor film 36 can emit light. As a result, the number of phosphor particles, which emit light, increases. Therefore, the phosphor film 36 with high brightness can be obtained (phosphor particles 36a filled in with black in Fig. 2 emit light). In addition, since the amount of expensive phosphor particles to be used are decreased, producing cost can be reduced.

[0021] In addition, fluoride particles, preferably such as  $\text{CaF}_2$ ,  $\text{MgF}_2$ , and  $\text{LiF}$ , or  $\text{SiO}_2$  particles is used as the ultraviolet-ray-transmittable particles in the embodiment 2, however, fluoride particles coated with  $\text{SiO}_2$  film may be used. It is preferable that the fluoride particles coated with  $\text{SiO}_2$  film are produced by a sol-gel method, a CVD method, a sputtering method, or the like. An example is shown in the case that  $\text{CaF}_2$  particles coated with  $\text{SiO}_2$  film are produced by a sol-gel method. First, a predetermined amount of  $\text{CaF}_2$  particles is added to solvent, which is a mixture of ethyl silicate, ethyl alcohol, hydrochloric acid with predetermined concentration, and isopropyl alcohol in predetermined amounts, respectively. After stirring for 30 minutes at room temperature, it is filtered with filter paper. Then, the filtered particles stand in the air at  $600^\circ\text{C}$  for

30 minutes, consequently, the  $\text{CaF}_2$  particles coated with  $\text{SiO}_2$  film can be obtained by baking it with holding temperature in the air at  $600^\circ\text{C}$  for one hour. It is preferable that the thickness of the  $\text{SiO}_2$  film is 1-10  $\mu\text{m}$ . The reason for covering  
5 the  $\text{CaF}_2$  particles with  $\text{SiO}_2$  film as mentioned above is to improve durability under plasma atmosphere.

[0022]

[Examples] Next, examples of the present invention are described in detail with comparative examples.

10 <Example 1> A phosphor paste was prepared by mixing 5 g of phosphor particles, 0.3 g of thermal-expansible microcapsules, and 4.2 g of vehicle. Phosphor particles for red [(Y, Gd)  $\text{BO}_3\text{:Eu}$ ] with a mean particle diameter of 3  $\mu\text{m}$ , specific gravity of  $5.02\text{ g/cm}^3$  were used as the phosphor  
15 particles. Microcapsules, which included a shell of acrylonitrile group polymer and enclosed hydrocarbon with low boiling point therein, with a mean particle diameter of 5-8  $\mu\text{m}$  were used as the thermal-expansible microcapsules. In addition, a mixture of  $\alpha$ -terpineol/ethyl cellulose, the ratio  
20 by weight of which was 95/5, was used as the vehicle. The above phosphor paste was printed on the center of an upper surface of a substrate of soda-lime glass having 2-inch square with a contact screen having 1-inch square by screen-printing. After drying for 10 minutes at  $150^\circ\text{C}$ , it was baked at  $520^\circ\text{C}$   
25 for 30 minutes to evaporate hydrocarbon with low boiling point,

and to burn resin components in the vehicle, the thermal-expansible microcapsules, and so on out. Consequently, a phosphor film was obtained. Thus, this phosphor film was obtained as an example 1.

5 [0023] <Example 2> A phosphor paste was prepared by mixing 5 g of phosphor particles, 0.6 g of thermal-expansible microcapsules, and 4.2 g of vehicle. A phosphor film was formed in the same manner as the above example 1 other than this preparation. Thus, this phosphor film was obtained as  
10 an example 2.

<Example 3> A phosphor paste was prepared by mixing 20 g of phosphor particles, 5 g of  $\text{CaF}_2$  particles, and 15 g of vehicle. The same compositions as the phosphor particles and the vehicle of the example 1 were used. The  $\text{CaF}_2$  particles had  
15 a mean particle diameter of 30  $\mu\text{m}$ . The above phosphor paste was dried and was baked in the same manner as the example 1, consequently, a phosphor film was formed on the glass substrate. Thus, this phosphor film was obtained as an example  
3.

20 <Example 4> A phosphor paste was prepared by mixing 9 g of phosphor particles, 1 g of  $\text{CaF}_2$  particles (mean particle diameter 30  $\mu\text{m}$ ), and 8.5 g of vehicle. A phosphor film was formed in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as  
25 an example 4.

[0024]<Example 5> A phosphor paste was prepared by mixing 10 g of phosphor particles, 5 g of  $\text{CaF}_2$  particles (mean particle diameter 30  $\mu\text{m}$ ), and 10 g of vehicle. A phosphor film was formed in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as an example 5.

<Example 6> A phosphor paste was prepared by mixing 10 g of phosphor particles, 10 g of  $\text{CaF}_2$  particles (mean particle diameter 30  $\mu\text{m}$ ), and 15 g of vehicle. A phosphor film was formed in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as an example 6.

<Example 7> A phosphor paste was prepared by mixing 10 g of phosphor particles, 5 g of  $\text{MgF}_2$  particles (mean particle diameter 30  $\mu\text{m}$ ), and 10 g of vehicle. A phosphor film was formed in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as an example 7.

[0025]<Example 8> A phosphor paste was prepared by mixing 10 g of phosphor particles, 10 g of  $\text{MgF}_2$  particles (mean particle diameter 30  $\mu\text{m}$ ), and 15 g of vehicle. A phosphor film was formed in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as an example 8.

<Example 9> A phosphor paste was prepared by mixing 10 g of

phosphor particles, 5 g of LiF particles (mean particle diameter 30  $\mu$ m), and 10 g of vehicle. A phosphor film was formed in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as an  
5 example 9.

<Example 10> A phosphor paste was prepared by mixing 10 g of phosphor particles, 10 g of LiF particles (mean particle diameter 30  $\mu$ m), and 15 g of vehicle. A phosphor film was formed in the same manner as the above example 3 other than this  
10 preparation. Thus, this phosphor film was obtained as an example 10.

[0026]<Example 11> A phosphor paste was prepared by mixing 20 g of phosphor particles, 5 g of SiO<sub>2</sub> particles (mean particle diameter 30  $\mu$ m), and 15 g of vehicle. A phosphor film  
15 was formed in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as an example 11.

<Example 12> A phosphor paste was prepared by mixing 9 g of phosphor particles, 1 g of SiO<sub>2</sub> particles (mean particle  
20 diameter 30  $\mu$ m), and 8.5 g of vehicle. A phosphor film was formed in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as an example 12.

[0027]<Example 13> A phosphor paste was prepared by mixing  
25 10 g of phosphor particles, 5 g of SiO<sub>2</sub> particles (mean

particle diameter 30  $\mu\text{m}$ ), and 10 g of vehicle. A phosphor film was formed in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as an example 13.

5 <Example 14> A phosphor paste was prepared by mixing 10 g of phosphor particles, 10 g of  $\text{SiO}_2$  particles (mean particle diameter 30  $\mu\text{m}$ ), and 15 g of vehicle. A phosphor film was formed in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as an  
10 example 14.

[0028] <Example 15> A phosphor paste was prepared by mixing 10 g of phosphor particles, 5 g of  $\text{CaF}_2$  particles coated with  $\text{SiO}_2$  film (mean particle diameter 30  $\mu\text{m}$ ), and 10 g of vehicle. The above  $\text{CaF}_2$  particles coated with  $\text{SiO}_2$  film was produced  
15 by a sol-gel method. Namely, 10 g of the same  $\text{CaF}_2$  particles as example 3 was added to 50 g of solvent, which was a mixture of 34.8% by weight of ethyl silicate, 50% by weight of ethyl alcohol, 6% by weight of hydrochloric acid (concentration 0.3%), and 9.2% by weight of isopropyl alcohol. After stirring  
20 for 30 minutes at room temperature, it was filtered with filter paper. Then, the filtered particles was dried in the air at 600°C for 30 minutes, consequently,  $\text{CaF}_2$  particles coated with  $\text{SiO}_2$  film were obtained by baking it at 600°C for one hour. The thickness of the  $\text{SiO}_2$  film was 1  $\mu\text{m}$ . The above  
25 phosphor paste was dried and was baked in the same manner as



the example 1, consequently, a phosphor film was formed on the glass substrate. Thus, this phosphor film was obtained as an example 15.

<Example 16> A phosphor paste was prepared by mixing 10 g of phosphor particles, 10 g of  $\text{CaF}_2$  particles coated with  $\text{SiO}_2$  film (mean particle diameter 30  $\mu\text{m}$ ), and 15 g of vehicle. A phosphor film was formed in the same manner as the above example 15 other than this preparation. Thus, this phosphor film was obtained as an example 16.

[0029]<Example 17> A phosphor paste was prepared by mixing 20 g of phosphor particles, 5 g of  $\text{CaF}_2$  particles (mean particle diameter 30  $\mu\text{m}$ , specific gravity 3.0  $\text{g}/\text{cm}^3$ ), and 15 g of vehicle. Phosphor particles for green [ $\text{Zn}_2\text{SiO}_4\text{:Mn}$ ] with a mean particle diameter of 3.6  $\mu\text{m}$ , specific gravity of 4.2  $\text{g}/\text{cm}^3$  were used as the phosphor particles. A mixture of  $\alpha$ -terpineol/ethyl cellulose, the ratio by weight of which was 95/5, was used as the vehicle. The above phosphor paste was printed on the center of an upper surface of an alumina substrate having 1-inch width and 2-inch length with a contact screen having 1-inch square by screen-printing. Next, it was dried at 150°C for 10 minutes. Then, it was baked at 520°C for 30 minutes to burn resin components in the vehicle out. Consequently, a phosphor film was obtained. Thus, this phosphor film was obtained as an example 17.

[0030]<Example 18> A phosphor paste was prepared by mixing

9 g of phosphor particles, 1 g of  $\text{CaF}_2$  particles (mean particle diameter 30  $\mu\text{m}$ ), and 8.5 g of vehicle. A phosphor film was formed in the same manner as the above example 17 other than this preparation. Thus, this phosphor film was obtained as  
5 an example 18.

<Example 19> A phosphor paste was prepared by mixing 10 g of phosphor particles, 5 g of  $\text{CaF}_2$  particles (mean particle diameter 30  $\mu\text{m}$ ), and 10 g of vehicle. A phosphor film was formed in the same manner as the above example 17 other than this  
10 preparation. Thus, this phosphor film was obtained as an example 19.

<Example 20> A phosphor paste was prepared by mixing 10 g of phosphor particles, 10 g of  $\text{CaF}_2$  particles (mean particle diameter 30  $\mu\text{m}$ ), and 15 g of vehicle. A phosphor film was formed  
15 in the same manner as the above example 17 other than this preparation. Thus, this phosphor film was obtained as an example 20.

<Example 21> A phosphor paste was prepared by mixing 10 g of phosphor particles, 5 g of  $\text{MgF}_2$  particles (mean particle  
20 diameter 30  $\mu\text{m}$ ), and 10 g of vehicle. A phosphor film was formed in the same manner as the above example 17 other than this preparation. Thus, this phosphor film was obtained as an example 21.

[0031]<Example 22> A phosphor paste was prepared by mixing  
25 10 g of phosphor particles, 10 g of  $\text{MgF}_2$  particles (mean

particle diameter 30  $\mu\text{m}$ ), and 15 g of vehicle. A phosphor film was formed in the same manner as the above example 17 other than this preparation. Thus, this phosphor film was obtained as an example 22.

5 <Example 23> A phosphor paste was prepared by mixing 10 g of phosphor particles, 5 g of LiF particles (mean particle diameter 30  $\mu\text{m}$ ), and 10 g of vehicle. A phosphor film was formed in the same manner as the above example 17 other than this preparation. Thus, this phosphor film was obtained as an  
10 example 23.

<Example 24> A phosphor paste was prepared by mixing 10 g of phosphor particles, 10 g of LiF particles (mean particle diameter 30  $\mu\text{m}$ ), and 15 g of vehicle. A phosphor film was formed in the same manner as the above example 17 other than this  
15 preparation. Thus, this phosphor film was obtained as an example 24.

[0032]<Example 25> A phosphor paste was prepared by mixing 5 g of phosphor particles, 0.3 g of thermal-expansible microcapsules, and 4.2 g of vehicle without using  
20 ultraviolet-ray-transmittable particles. A phosphor film was formed in the same manner as the above example 17 other than this preparation. Thus, this phosphor film was obtained as an example 25.

<Example 26> A phosphor paste was prepared by mixing 5 g of  
25 phosphor particles, 0.6 g of thermal-expansible

microcapsules, and 4.2 g of vehicle without using ultraviolet-ray-transmittable particles. A phosphor film was formed in the same manner as the above example 17 other than this preparation. Thus, this phosphor film was obtained  
5 as an example 26.

[0033]<Example 27> A phosphor paste was prepared by mixing 3.7 g of phosphor particles, 0.1 g of acrylic resin fine particles (mean particle diameter 3  $\mu$ m, Soken Chemical & Engineering Co., Ltd), and 3.5 g of vehicle. A phosphor film  
10 was formed in the same manner as the above example 17 other than this preparation. Thus, this phosphor film was obtained as an example 27.

<Example 28> A phosphor paste was prepared by mixing 2.9 g of phosphor particles, 0.3 g of acrylic resin fine particles  
15 (mean particle diameter 3  $\mu$ m, Soken Chemical & Engineering Co., Ltd), and 3.0 g of vehicle. A phosphor film was formed in the same manner as the above example 17 other than this preparation. Thus, this phosphor film was obtained as an example 28.

<Example 29> A phosphor paste was prepared by mixing 2.1 g of phosphor particles, 0.5 g of acrylic resin fine particles  
20 (mean particle diameter 3  $\mu$ m, Soken Chemical & Engineering Co., Ltd), and 2.0 g of vehicle. A phosphor film was formed in the same manner as the above example 17 other than this  
25 preparation. Thus, this phosphor film was obtained as an

example 29.

[0034]<Comparative Example 1>

A phosphor paste was prepared by mixing 20 g of phosphor particles, and 10 g of vehicle. A phosphor film was formed  
5 in the same manner as the above example 3 other than this preparation. Thus, this phosphor film was obtained as a comparative example 1.

<Comparative Example 2> A phosphor paste was prepared by mixing 20 g of phosphor particles, and 10 g of vehicle. A  
10 phosphor film was formed in the same manner as the above example 17 other than this preparation. Thus, this phosphor film was obtained as a comparative example 2.

[0035]<Comparative Test 1 and evaluation> Table 1 shows the amounts of addition of phosphor particles,  
15 ultraviolet-ray-transmittable particles, thermal-expansible microcapsule, and vehicle of the examples 1-16, and the comparative example 1. In addition, the void rates of the phosphor films of examples 1-2 and the comparative example 1 were calculated as follows, and were  
20 shown in Table 1. First, the area, the film thickness, and the weight after the baking process of the phosphor film are measured, and the density of the phosphor film was calculated. Next, a value W was obtained by dividing the density of the phosphor film by the density of the phosphor particles, and  
25 then the void rate was obtained by multiplying a value, which

was obtained by subtracting W from 1, by 100.

[0036] Additionally, the rate that the voids within the respective particles, and the ultraviolet-ray-transmittable particles occupy in the phosphor film of examples 3-16 were  
5 calculated as follows, and are shown in Table 1. First, the area, the film thickness, and the weight after the baking process of the phosphor film were measured, and the weight of the ultraviolet-ray-transmittable particles contained in the phosphor film was calculated according to the mixture  
10 ratio of the phosphor particles and the ultraviolet-ray-transmittable particles. Y was obtained by dividing a value X, which was obtained by subtracting the weight of the ultraviolet-ray-transmittable particles from the above weight after the baking process, by the volume of  
15 the phosphor film. In addition, a value Z was obtained by dividing the value Y by the density of the phosphor particles, and then the rate that the voids within the respective particles, and the ultraviolet-ray-transmittable particles occupy was obtained by multiplying a value, which was obtained  
20 by subtracting Z from 1, by 100. Further, the glass substrates (the glass substrate on the surface of which the phosphor film was formed) of the examples 1-16 and the comparative example 1 were put into a darkroom, and the ultraviolet rays (wavelength: 254nm) by a low-pressure mercury lamp were  
25 irradiated to the above phosphor films, and the brightness

of phosphor films was measured. In this evolution, the brightness of the phosphor film was defined as a value of saturated brightness with increasing the thickness of the phosphor film. Additionally, the brightness of the examples 5 1-16 was a relative value for the brightness of the comparative example 1 as 100. Table 1 shows these values.

[0037]

[Table 1]

	Phosphor particle		Ultraviolet-ray-transmittable particle		Thermal-expandable microcapsules (g)	Vehicle (g)	Void rate (%)	Rate that voids within respective particles, and ultraviolet-ray-transmittable particles occupy (%)	Brightness
	g	Color	Type	g					
Example 1	5	Red	-	-	0.3	4.2	40	-	110
Example 2	5	Red	-	-	0.6	4.2	70	-	110
Example 3	20	Red	CaF <sub>2</sub>	5	-	15.0	-	50	107
Example 4	9	Red	CaF <sub>2</sub>	1	-	8.5	-	40	107
Example 5	10	Red	CaF <sub>2</sub>	5	-	10.0	-	65	107
Example 6	10	Red	CaF <sub>2</sub>	10	-	15.0	-	80	105
Example 7	10	Red	MgF <sub>2</sub>	5	-	10.0	-	65	110
Example 8	10	Red	MgF <sub>2</sub>	10	-	15.0	-	80	108
Example 9	10	Red	LiF	5	-	10.0	-	65	112
Example 10	10	Red	LiF	10	-	15.0	-	80	110
Example 11	20	Red	SiO <sub>2</sub>	5	-	15.0	-	60	107
Example 12	9	Red	SiO <sub>2</sub>	1	-	8.5	-	55	107
Example 13	10	Red	SiO <sub>2</sub>	5	-	10.0	-	65	107
Example 14	10	Red	SiO <sub>2</sub>	10	-	15.0	-	75	105
Example 15	10	Red	CaF <sub>2</sub> particles coated with SiO <sub>2</sub> film	5	-	10.0	-	65	105
Example 16	10	Red	CaF <sub>2</sub> particles coated with SiO <sub>2</sub> film	10	-	15.0	-	80	103
Comparative Example 1	20	Red	-	-	-	10.0	30	-	100



[0038] Table 1 clearly shows the brightness of the phosphor films of examples 1-16 was improved 3-12% as compared with the phosphor film of the comparative example 1.

[0039] <Comparative Test 2 and evaluation> Table 2 shows the amounts of addition of phosphor particles, ultraviolet-ray-transmittable particles, resin beads, thermal-expansible microcapsule, and vehicles of the examples 17-29, and the comparative example 2, and also shows the rate that the voids within the respective particles, and the ultraviolet-ray-transmittable particles occupy in the phosphor film. In addition, the brightness of examples 17-29 and the comparative example 2 was measured as follows. First, the alumina substrate, which the phosphor film was formed on, was put into the vacuum chamber, and then the vacuum pump decompressed the vacuum chamber at  $2 \times 10^{-2}$  or less Torr. Further, vacuum ultraviolet rays (wavelength: 146nm) by an excimer lamp (USHIO Inc.: UER20H146) were irradiated to the above phosphor films, and the brightness of the phosphor films was measured. In this evolution, the brightness of the phosphor film was defined as a value of a saturated brightness with increasing the thickness of the phosphor film. Additionally, the brightness of the examples 17-29 was a relative value for the brightness of the comparative example 2 as 100. Table 2 shows these values.

[0040]

[Table 2]

	Phosphor particle		Ultraviolet-ray-transmittable particle		Resin beads (g)	Thermal-expandable microcapsules (g)	Vehicle (g)	Void rate (%)	Rate that voids within respective particles, and ultraviolet-ray-transmittable particles occupy (%)	Brightness
	g	Color	Type	g						
Example 17	20	Green	CaF <sub>2</sub>	5	-	-	15.0	40	50	115
Example 18	9	Green	CaF <sub>2</sub>	1	-	-	8.5	70	40	115
Example 19	10	Green	CaF <sub>2</sub>	5	-	-	10.0	-	65	115
Example 20	10	Green	CaF <sub>2</sub>	10	-	-	15.0	-	80	112
Example 21	10	Green	MgF <sub>2</sub>	5	-	-	10.0	-	65	117
Example 22	10	Green	MgF <sub>2</sub>	10	-	-	15.0	-	80	115
Example 23	10	Green	LiF	5	-	-	10.0	-	65	120
Example 24	10	Green	LiF	10	-	-	15.0	-	80	118
Example 25	5	Green	-	-	-	0.3	4.2	40	-	102
Example 26	5	Green	-	-	-	0.6	4.2	70	-	105
Example 27	3.7	Green	-	-	0.1	-	3.5	40	-	105
Example 28	2.9	Green	-	-	0.3	-	3.0	60	-	110
Example 29	2.1	Green	-	-	0.5	-	2.5	80	-	107
Comparative Example 2	10	Green	-	-	-	-	10.0	30	-	100

[0041] Table 2 clearly shows the brightness of the phosphor films of examples 17-29 was improved 2-20% as compared with the phosphor film of the comparative example 2.

[0042]

5 [Effect of the Invention] As mentioned above, a phosphor film according to the present invention includes a number of phosphor particles and voids formed within these phosphor particles, wherein the voids occupy 40-80% in the phosphor film where it is defined as 100% that the phosphor particles  
10 completely occupy the phosphor film without any voids. Accordingly, ultraviolet rays generated by a plasma discharge meet not only phosphor particles in the surface of the phosphor film but also particles inside the phosphor film. As a result, the phosphor particles inside the phosphor film  
15 can also emit light, and a phosphor film with high brightness can be obtained. In addition, since the phosphor film has a number of voids, the amount of expensive phosphor particles to be used is decreased. Therefore, producing cost can be reduced.

20 [0043] In addition, a phosphor film includes a number of phosphor particles and a number of ultraviolet-ray-transmittable particles positioned within these phosphor particles, wherein voids formed within the respective particles, and the ultraviolet-ray-transmittable  
25 particles occupy 40-80% in the phosphor film where it is

defined as 100% that the phosphor particles completely occupy the phosphor film without any voids. Accordingly, since ultraviolet rays generated by a plasma discharge can pass through the ultraviolet-ray-transmittable particles, the ultraviolet rays meet not only phosphor particles in the surface of the phosphor film but also particles inside the phosphor film. As a result, the phosphor particles inside the phosphor film can also emit light, a phosphor film with high brightness can be obtained. Additionally, since the predetermined amount of expensive phosphor particles can be replaced with relatively cheap ultraviolet-ray-transmittable particles, producing cost can be reduced.

[0043] Further, in the case that the ultraviolet-ray-transmittable particles are fluoride particles or  $\text{SiO}_2$  particles, in particular, in the case that the fluoride particles are any of  $\text{CaF}_2$ ,  $\text{MgF}_2$ , and  $\text{LiF}$ , the above effects can be remarkably obtained. Furthermore, in the case that the ultraviolet-ray-transmittable particles are fluoride particles coated with  $\text{SiO}_2$  film, durability of this fluoride particle under plasma atmosphere can be improved. Moreover, when a phosphor film is formed by a paste comprising phosphor particles, ultraviolet-ray-transmittable particles, thermal expansion characteristic macroscopic capsules or resin fine particles, and a mixture of resin and

solvent in predetermined amounts, respectively, it is possible to improve the workability of producing a phosphor film, and producing cost can be further reduced. Particularly, when the phosphor is formed on inner surfaces of a cell  
5 surrounded by ribs on or above a substrate of a fluorescence display, such as a PDP, it is possible to easily produce a fluorescence display, such as a PDP. This can remarkably contribute in the related technical field.

10 [Brief Description of the Drawings]

[Fig. 1] Fig. 1 is a sectional view of a prime construction in a PDP showing a phosphor structure according to an embodiment 1 of the present invention.

[Fig. 2] Fig. 2 is a sectional view corresponding to Fig. 1  
15 showing a phosphor structure according to an embodiment 2 of the present invention.

[Fig. 3] Fig. 3 is a sectional view corresponding to Fig. 1 showing a conventional phosphor structure.

[Explanation of reference letters or numerals]

20 16 and 36 Phosphor film

16a and 36a Phosphor particle

16b and 36c Void

36b Ultraviolet-ray-transmittable particle